

PATENT SPECIFICATION

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(54) CATALYTIC POLYMERIZATION OF OLEFINS

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, a Japanese company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka-Shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for polymerizing an olefinically unsaturated hydrocarbon, which comprises polymerizing the olefin in the presence of a catalyst which is capable of producing highly stereospecific olefin polymers, and which has good catalytic activity.

It is well known that an olefin polymer may be obtained in high yield by polymerizing olefin using a catalyst comprising a compound of a transition metal of Groups IV to VI of the Periodic Table and a metal or an organometallic compound of the Groups I to III of the Periodic Table, i.e., a so-called Ziegler-Natta catalyst and that the polymers produced by the above process are generally in the form of a polymer slurry comprising amorphous polymers as by-products in addition to the desired crystalline olefin polymer.

In such a polymerization process, the bulk density of the olefin polymers produced generally affects the productivity of polymer production process and, therefore, an improvement in the bulk density is desirable in order to increase the efficiency of the reactor used for the polymerization.

Also, in olefin polymers, the stereospecificity of the polymers greatly affects the mechanical properties of moulded articles such as films, fibres and other articles prepared from the polymers.

Furthermore, the production as by-products of amorphous polymers which are of commercially less value for industrial utilization results in the loss of monomer used for the polymerization and, in addition, necessitates equipment for the removal of such amorphous polymers, thereby making the polymerization process uneconomical and disadvantageous

from the industrial standpoint. Accordingly, it is apparent that a polymerization process capable of producing polymers which are substantially free from amorphous polymer or which contain only a minimum amount of amorphous polymer is industrially advantageous.

However, the polymer obtained by such polymerization processes contains a residual catalyst which subsequently causes various problems such as instability and colouration of the olefin polymers, thus requiring equipment for the removal of the residual catalyst.

The above disadvantages associated with the conventional catalyst can be improved if the polymerization activity of the catalyst, i.e., unit weight of olefin polymer produced per unit weight of the catalyst used for the olefin polymerization, can be increased, whereby the equipment required for the removal of the residual catalyst can be eliminated and the cost for the production of olefin polymer can be reduced.

A typical solid catalyst which has been conventionally used for the polymerization of olefins is titanium trichloride. The titanium trichloride catalyst is generally prepared from titanium tetrachloride by (1) reduction with hydrogen, (2) reduction with aluminium metal at high temperatures, (3) reduction with an organoaluminium compound at approximately room temperature, or the like. It is also known that an organomagnesium compound, for example, a Grignard reagent, can be used as a reducing agent for the reduction of titanium tetrachloride.

Titanium trichloride obtained by the organoaluminium reduction of titanium tetrachloride has a β -type crystal structure, and the polymer produced by polymerizing olefin using a catalyst comprising a combination of the above β -type titanium trichloride and an organoaluminium compound has a drawback because of its low stereospecificity, i.e., having a 70 to 80% content which is insoluble in boiling heptane.

Furthermore, the catalyst obtained by reducing titanium tetrachloride using an organo-

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magnesium compound has a low catalytic activity when used in the polymerization of α -olefins, and the stereospecificity of the resultant polymers is extremely poor. Therefore, such a catalyst is not suitable for use in the polymerization of α -olefins.

An object of the present invention is to provide an improved process for obtaining a polyolefin having a high stereospecificity and containing a minimum amount of amorphous polymers.

As a result of extensive research into a catalyst having a high catalytic activity and which is capable of producing a highly stereospecific polymer, we have found that a catalyst prepared by reacting a transition metal compound with an organomagnesium compound and treating the resultant solid with a Lewis acid has a surprisingly increased catalytic activity for the polymerization of olefins and that the stereospecificity of the resultant polymers is greatly improved.

The process of the invention comprises polymerizing an olefinically unsaturated hydrocarbon in the joint presence of

(1) a catalyst obtained by reacting at a temperature of from -80 to 100°F , a transition metal compound represented by the formula



wherein Me represents a transition metal of Group IVb or Vb of the Periodic Table, X represents a halogen atom selected from fluorine, chlorine, bromine and iodine atoms, Y represents an oxygen atom or an organic radical selected from an alkyl group having 1 to 6 carbon atoms and alkoxy groups having 1 to 9 carbon atoms, n represents an integer equivalent to or less than the maximum valence of said transition metal, and m represents a number having a positive value of from 0 to n (with the proviso that when Y is oxygen, then m is 1 and the number of said halogen atoms is $n-2$) with an organomagnesium compound, treating the resultant reaction solid with a Lewis acid and isolating the treated solid from the reaction mixture and

(2) as an activator for the catalyst, an organo-aluminum compound represented by the formula



wherein Z represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, X represents a halogen atom as defined above, and n represents a number having a positive value of from 1.5 to 3.

The transition metal compounds of the above general formula (I) and which may be used in preparing the catalyst include, for example, a titanium tetrachloride or titanium tetrabromide;

a tetraalkoxy titanium such as tetramethoxy titanium, tetraethoxy titanium, tetrapropoxy titanium or tetrabutoxy titanium; an alkoxy titanium halide such as triethoxy titanium chloride, tripropoxy titanium chloride, tributoxy titanium chloride, diethoxy titanium dichloride, dipropoxy titanium dichloride, dibutoxy titanium dichloride, ethoxy titanium trichloride, propoxy titanium trichloride, butoxy titanium trichloride or dibutoxyethoxy titanium chloride; a tetravalent titanium compound such as methyl titanium trichloride; a vanadium compound such as vanadium tetrachloride, vanadium tetrabromide, vanadium oxychloride or vanadium oxybromide; zirconium chloride; zirconium bromide; niobium chloride; tantalum chloride; and tantalum bromide.

The organomagnesium compounds which may be used in preparing the catalyst can be prepared by any known process. A particularly easy process for preparing the organomagnesium compound is according to a Grignard method, in which magnesium in a metallic state is reacted with an organic compound substituted with one halogen atom which is represented by the formula $\text{R}-\text{X}$ wherein R represents a hydrocarbon radical such as an alkyl group having from 1 to 18 carbon atoms, an aryl group having from 6 to 18 carbon atoms and X represents a halogen atom such as a fluorine, bromine, chlorine or iodine atom. Most Grignard reactions can be carried out in the presence of a large quantity of an ether, e.g., diethyl ether or di- n -butyl ether. The Grignard reagent used in the above-described method can generally be expressed by the formula RMgX , but the actual reagent which undergoes the reaction includes a diethyl ether adduct dissolved in an excessive amount of diethyl ether. The ether solvate of the organomagnesium compound may be employed as it is in the preparation of the catalyst according to the present invention.

The organomagnesium compounds may also be prepared by employing an inert diluent which does not react with the Grignard reagent, for example, an inert hydrocarbon such as hexane, heptane, octane, decalin, benzene, toluene, xylene or ligroin or tertiary amine such as dimethylaniline or as a solvent or as a part of a solvent. The organomagnesium compounds thus prepared may be used in the preparation of the catalyst according to the present invention.

In addition, a compound represented by the formula $\text{R}'\text{MgR}^1$ or $\text{R}'\text{MgOR}^1$ in which R' and R^1 each represents a hydrocarbon radical such as an alkyl group or an aryl group may also be used in the process of the present invention as an organomagnesium compound.

The reaction between a compound of a transition metal of Group IVb or Vb of the

Periodic Table and an organomagnesium compound can be carried out according to any well-known procedure, for example, by adding the organomagnesium compound to the transition metal compound diluted with or suspended in an inert diluent or *vice versa*, i.e., adding the transition metal compound to the organomagnesium compound.

The organomagnesium compound may be used in an amount of from 0.5 to 3 moles, preferably from 0.6 to 2 moles, per mole of the transition metal compound; the reaction temperature is from -80 to 100°C, preferably from -30 to 80°C. After completion of the reaction, the resultant precipitate can either be separated from the reaction medium, washed with an inert diluent and dried or be subjected as it is to subsequent treatment with a Lewis acid.

The reaction solid thus obtained may be employed in the polymerization of α -olefins in the presence of an organometal compound, particularly an organoaluminum compound, as an activator. However, the catalytic activity exhibited by the above-obtained reaction solid without further treatment is very low and the stereospecificity of the resultant polymer is extremely inferior.

According to the present invention, a catalyst obtained by treating the above-obtained reaction solid with a Lewis acid exhibits a highly increased catalytic activity on the polymerization of α -olefins, and also the stereospecificity of the resultant polymers is markedly improved whereby an economically advantageous process for polymerizing α -olefins is provided. It has not yet been confirmed what kind of chemical reactions occur or what kind of physical changes the reaction solid undergoes by the treatment with a Lewis acid.

The Lewis acids which can be used in the above treatment include halides and oxyhalides of metals of Groups II to VIII of the Periodic Table, phosphorus and boron. Of these Lewis acids, particularly preferred examples are ZnCl_2 , CdCl_2 , BF_3 , BCl_3 , BBr_3 , AlCl_3 , EtAlCl_2 , Et_2AlCl , SiCl_4 , SnCl_4 , TiCl_4 , TiBr_4 , ZrCl_4 , VCl_3 , VCl_4 , VOCl_3 , WCl_6 , MnCl_4 , CoCl_2 , NiCl_2 , MgCl_2 , PCl_5 , POCl_3 and TeCl_4 .

The amount of the Lewis acid used is not critical. However, as will be apparent to one skilled in the art, the amount can be determined from the standpoints of efficiency and cost. Use of too small amount of the Lewis acid brings about almost no effect and too large amount gives no additional advantage: it is preferable to use from 0.1 to 10 moles of the Lewis acid per 1 g of the reaction solid to be treated. The Lewis acid may be employed either alone or as a mixture of two or more Lewis acids.

The treatment with the Lewis acid may be carried out according to the following

procedure. The reaction solid can be treated with a pure Lewis acid, a Lewis acid diluted with an inert diluent such as *n*-hexane, *n*-heptane, cyclohexane, methylcyclohexane, benzene, toluene or xylene or a gaseous Lewis acid diluted with an inert gas such as helium, argon or nitrogen, at a temperature of about from -30 to 100°C, preferably from 0 to 80°C. The treatment may be conducted for a period of more than 5 minutes, preferably from 30 minutes to 5 hours, but in cases where the treatment is effected using a ball mill, the period of treatment will sometimes be prolonged to a period of from several days to several weeks. The treated reaction solid is then isolated from the reaction mixture.

When the reaction solid in a form of a solution or a suspension is subjected to the treatment with the Lewis acid, the treated reaction solid is subsequently separated from the reaction medium by filtration, decantation or the like, washed with an inert diluent such as *n*-hexane, *n*-heptane, cyclohexane, methylcyclohexane, benzene, toluene or xylene to remove any residual Lewis acid, by-products and the like, optionally followed by drying, to obtain the catalyst used in the present invention.

Analyses of the thus-obtained catalyst revealed that it contains a magnesium compound which does not have reductivity as an organomagnesium compound, and a reduced transition metal compound. The composition of the catalyst varies widely according to properties of various reactants and the amount thereof.

In the organoaluminum compounds represented by the general formula (II) and used as an activator, X represents preferably a chlorine atom. Preferred examples of the organoaluminum compounds are dialkyl aluminum halides and trialkyl aluminums, particularly diethyl aluminum chloride and triethyl aluminum.

The halogen content of the organoaluminum compound used as an activator should be selected depending upon the type of the transition metal compound used in the preparation of the catalyst. The combination of the transition metal compound and the organoaluminum compound has an important influence upon the catalytic activity of the resultant catalysts and the stereospecificity of the resultant polymers.

The molar ratio of the solid catalyst and the organoaluminum activator compound used for the polymerization of the hydrocarbon can vary widely from 1:0.01 to 1:1000, preferably from 1:0.1 to 1:100.

The concentration of the organoaluminum compound in the polymerization system varies widely from an extremely low concentration, i.e., 0.1 mmole/litre, to an infinitely high concentration, i.e., the absence of diluent.

The monomers which may be polymerized

according to the present invention are olefinically unsaturated hydrocarbons, preferably α -olefins, having from 2 to 15 carbon atoms which can be straight or branched chain hydrocarbons. Also, the α -olefinic hydrocarbons may contain aromatic hydrocarbon groups and/or alicyclic hydrocarbon groups. Typical examples of the α -olefins are ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1, decene-1, 3-methylpentene-1, 4-methylpentene-1, vinylcyclohexene and styrene.

The process of this invention can be used for both homopolymerization and copolymerization (including block copolymerization) of olefins. In copolymerization, the solid catalyst is contacted with two or more different types of olefin in an admixed state to obtain a copolymer. In employing the solid catalyst in the copolymerization of two different types of olefin monomer, it is preferred that one of the two olefin monomers is used in a proportion of less than about 10 mole% with respect to the other olefin monomer in order to obtain a highly stereospecific copolymer.

The polymerization may be carried out by suspending the catalyst in a monomer or monomers or in a solution of a monomer or monomers dissolved in an inert diluent such as an aromatic or alicyclic hydrocarbon such as benzene, toluene, hexane, heptane, octane or decalin or the polymerization may be conducted in the gaseous phase without using any liquid diluent. The polymerization may be carried out at a temperature of from 0 to 200°C, preferably from 20 to 150°C, for from 1 minute to 20 hours. The polymerization pressure is not critical, but a pressure of from 1 to about 50 atmospheres is preferred. The molecular weight of the resultant polymer can usually be controlled by hydrogen.

The present invention is illustrated in greater detail in the following Examples in which, unless otherwise indicated, all parts, percentages, ratios and the like are by weight.

Example 1.

A. Preparation of Organomagnesium Compound

A 300 ml flask equipped with a stirrer, a condenser and a dropping funnel was charged with 4.9 g (0.2 moles) of magnesium powder, and the flask was heated at 120°C for 2 hours while introducing argon into the reaction system completely to remove moisture on the inner wall of the flask and the surface of the magnesium. 21 ml (0.2 moles) of *n*-butyl chloride and 100 ml of *n*-butyl ether were charged into the dropping funnel and added dropwise to the magnesium over a period of 1 hour while maintaining the temperature of the reaction system at 90°C. After completion of the addition, the mixture was allowed to react further at 90°C

for an additional hour followed by cooling to room temperature.

B. Preparation of Reaction Solid

A 500 ml flask equipped with a stirrer and a dropping funnel was purged with argon, and 250 ml of hexane and 8 ml of titanium tetrachloride were charged into the flask. 50 ml of the organomagnesium compound prepared as described in A above were then charged into the dropping funnel and added dropwise to the titanium tetrachloride solution over a period of 2 hours while maintaining the reaction temperature at 0 to 50°C. After completion of the addition, the reaction was further continued for 3 hours. After the reaction mixture had been allowed to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 100 ml portions of hexane followed by drying to obtain an ochre reaction solid.

C. Preparation of Catalyst

10 Grams of the reaction solid prepared as described in B above were charged into a 100 ml flask purged with argon, and 20 ml of hexane and 15 ml of titanium tetrachloride were also charged into the flask. The resultant mixture was stirred at 70°C for 2 hours to treat the reaction solid with the titanium tetrachloride solution. The reaction mixture was cooled to room temperature and allowed to stand to settle the precipitate followed by removing the supernatant. The resultant precipitate was washed five times with 50 ml portions of hexane and dried to obtain a brown catalyst.

D. Polymerization of Ethylene

A 1-litre electromagnetic induction stainless steel autoclave equipped with a stirrer was purged with nitrogen and charged with 500 ml of dried *n*-heptane, 5 mmoles of triethyl aluminium and 10.0 mg of the catalyst prepared as described in C above. The autoclave was heated at 90°C while stirring. Ethylene was introduced into the autoclave to a partial pressure of hydrogen of 8 Kg/cm² and then to a total pressure of 15 Kg/cm². After 2 hours, any residual monomer was removed to recover 48 g of a polyethylene. The total amount of the polyethylene produced per 1 g of the catalyst was 4800 g.

Ethylene was polymerized in the same manner as described above but using 5 mmoles of diethyl aluminium chloride as an organoaluminium compound to obtain 103 g of a polyethylene. The total amount of the polyethylene produced per 1 g of the catalyst was 10300 g.

E. Polymerization of Propylene — (1)

A 5-litre electromagnetic stainless steel

autoclave equipped with a stirrer was purged with nitrogen and charged with 4.5 g of triethyl aluminium and 100 mg of the catalyst prepared as described in C above. Hydrogen was introduced into the autoclave to a pressure corresponding to a partial pressure of 0.53 Kg/cm². 1.4 Kg of liquid propylene was then introduced into the autoclave under pressure and polymerized while stirring and maintaining the autoclave at a temperature of 60°C for a period of 2 hours. After completion of the polymerization, unreacted propylene was removed, and 2 litres of methanol were added to the polymerization system to decompose the catalyst. The polypropylene thus obtained was separated by filtration using a Buchner funnel and dried at 60°C under reduced pressure to obtain 685 g of a polypropylene. The total amount of the polypropylene produced per 1 g of the catalyst was 6850 g. The polymer content which was insoluble in boiling heptane in the resultant polymer was found to be 82.6%.

F. Polymerisation of Propylene — (2)

A 5-litre electromagnetic stainless steel autoclave equipped with a stirrer was purged with nitrogen and charged with 1.5 litre of dried *n*-heptane, 4.5 g of diethyl aluminium chloride and 600 mg of the catalyst prepared as described in C above. Hydrogen was introduced into the autoclave to a pressure corresponding to a partial pressure of 0.16 Kg/cm². The temperature in the autoclave was then elevated to 70°C, and propylene was introduced into the autoclave to a total pressure of 6 Kg/cm² and polymerized while keeping the pressure at 6 Kg/cm² by introducing a propylene monomer for 2 hours. After completion of the polymerization, unreacted propylene was purged, and 100 ml of butanol were added to the polymerization system to decompose the catalyst. The polymer thus obtained was separated by filtration using a Buchner funnel, washed three times with 0.5-litre portions of heptane and dried at 60°C under reduced pressure to obtain 375 g of a solid polymer. The filtrate was subjected to steam distillation to remove heptane and then dried at 60°C under reduced pressure to recover 82 g of amorphous polymers produced as by-products. Therefore, the total amount of the polypropylene produced per 1 g of the catalyst was 762 g. Further, 45 g of the polymer which was insoluble in boiling heptane was recovered from the resultant solid polymer. This indicates that the polymer content which is insoluble in boiling heptane was 72.2%.

Comparative Example 1.

A. Polymerization of Ethylene

Ethylene was polymerized in the same manner as described in Example 1, D but using 10.0 mg of the reaction solid prepared

as described in Example 1, B. When triethyl aluminium was used as an organoaluminium compound, 10 g of a polyethylene were obtained indicating that the total amount of the polyethylene produced per 1 g of the catalyst was 1000 g. On the other hand, when diethyl aluminium chloride was used for polymerization, 88 g of a polyethylene were obtained, indicating that the total amount of the polyethylene produced per 1 g of the catalyst was 8800 g.

B. Polymerization of Propylene — (1)

Propylene was polymerized in the same manner as described in Example 1, B but using 300 mg of the reaction solid prepared as described in Example 1, B to obtain 97 g of a polypropylene. In this procedure, the total amount of the polypropylene produced per 1 g of the catalyst was 323 g, and the polymer content which was insoluble in boiling heptane in the resultant polymer was found to be 38.5%.

C. Polymerization of Propylene — (2)

Propylene was polymerized in the same manner as described in Example 1, F but using 600 g of the reaction solid prepared as described in Example 1, B to obtain 130 g of a solid polymer and 49 g of amorphous polymers. The total amount of the polypropylene produced per 1 g of the catalyst was 299 g, and the polymer content which was insoluble in boiling heptane in the resultant polymer was found to be 65.0%.

Example 2.

A. Preparation of Organomagnesium Compound

In the same manner as described in Example 1, A, a mixture of 21 ml of *n*-butyl chloride, 60 ml of *n*-butyl ether and 100 ml of *n*-heptane was added dropwise to 4.9 g of magnesium powder at a temperature of 90°C over a period of 2 hours. The reaction was further continued for an additional hour following by allowing the reaction mixture to stand to obtain an organomagnesium compound.

B. Preparation of Reaction Solid

In the same manner as described in Example 1, B, a solution of 8 ml of titanium tetrachloride in 50 ml of *n*-heptane was added dropwise to 125 ml of the organomagnesium compound prepared as described in A above at a temperature of 0 to 50°C over 2 hours. The reaction was further continued at room temperature for 3 additional hours. After the reaction mixture had been allowed to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 100 ml portions of *n*-heptane and dried to obtain a brown reaction solid.

C. Preparation of Catalyst

5 T 10 g of the reaction solid prepared as described in B above were added 25 ml of *n*-heptane and 15 ml of titanium tetrachloride, and the resultant mixture was allowed to react at a temperature of 50°C for a period of 2 hours followed by allowing the mixture to cool to room temperature. The supernatant was removed, and the resultant precipitate was washed five times with 50 ml portions of *n*-heptane and dried to obtain a brownish purple catalyst.

10 Each of ethylene and propylene was polymerized in the same manner as described in Example 1 using the thus-obtained catalyst. The results obtained are shown in Table 1 below.

Comparative Example 2.

20 Each of ethylene and propylene was polymerized in the same manner as described in Comparative Example 1 but using the reaction solid prepared as described in Example 2, B. The results obtained are shown in Table 2 below.

Example 3.

A. Preparation of Reaction Solid

25 In the same manner as described in Example 1, B, 20 ml of a solution of the organomagnesium compound prepared as described in Example 1, A was added dropwise to a solution of 10 ml of titanium tetrabutoxide in 200 ml of hexane at 0 to 5°C over 1 hour. The reaction was further continued at room temperature for 3 hours. After the reaction mixture had been allowed to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 100 ml portions of hexane and dried to obtain a yellowish brown reaction solid.

B. Preparation of Catalyst

40 To 5 g of the reaction solid as above obtained in A were added 15 ml of hexane and 10 ml of titanium tetrachloride, and the resultant mixture was allowed to react at a temperature of 70°C for 2 hours. After allowing the mixture to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 50 ml portions of hexane and then dried to obtain a brown reaction solid.

Each of ethylene and propylene was polymerized in the same manner as described in Example 1 but using the thus-obtained catalyst. The results obtained are shown in Table 1 below. 55

Comparative Example 3.

Each of ethylene and propylene was polymerized in the same manner as described in Comparative Example 1 but using the reaction solid prepared as described in Example 3, A. The results obtained are shown in Table 2 below. 60

Example 4.

A. Preparation of Reaction Solid

65 In the same manner as described in Example 1, B, 40 ml of a solution of the organomagnesium compound prepared as described in Example 1, A was added dropwise to a solution of 5.5 ml of vanadium oxytrichloride in 250 ml of hexane at 0 to 5°C over 2 hours. The reaction was further continued at room temperature for 3 additional hours. After allowing the reaction mixture to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 100 ml portions of hexane and dried to obtain a pale green reaction solid. 70 75

B. Preparation of Catalyst

80 To 5 g of the reaction solid as obtained above in A were added 20 g of hexane and 10 ml of titanium tetrachloride, and the resultant mixture was allowed to react at 70°C for 2 hours. After allowing the reaction mixture to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 50 ml portions of hexane and dried to obtain a dark green catalyst. 85 90

Each of ethylene and propylene was polymerized in the same manner as described in Example 1 using the thus-obtained catalyst. The results obtained are shown in Table 1 below. 95

Comparative Example 4.

Each of ethylene and propylene was polymerized in the same manner as described in Comparative Example 1 but using the reaction solid prepared as described in Example 4, A. The results obtained are shown in Table 2 below. 100

TABLE 1

Example	Polymerization method	Organoaluminium compound used in polymerization	Total amount of polymer produced per 1 g of catalyst	Total content of boiling heptane insoluble material
			(g)	(%)
2	Polymerization of ethylene	Diethyl aluminium chloride	13,100	—
	Polymerization of propylene-(1)	Diethyl aluminium chloride	1,790	62.5
		Triethyl aluminium	6,000	78.6
3	Polymerization of ethylene	Diethyl aluminium chloride	12,000	—
		Triethyl aluminium	6,350	—
	Polymerization of propylene-(1)	Diethyl aluminium chloride	1,920	76.6
Triethyl aluminium		4,340	72.5	
4	Polymerization of ethylene	Triethyl aluminium	6,600	—
	Polymerization of propylene-(1)	Triethyl aluminium	812	66.9

TABLE 2

Comparative Example	Polymerization method	Organoaluminium compound used in polymerization	Total amount of polymer produced per 1 g of catalyst	Total content of boiling heptane insoluble material
			(g)	(%)
2	Polymerization of ethylene	Diethyl aluminium chloride	9,100	—
	Polymerization of propylene-(1)	Diethyl aluminium chloride	1,210	21.1
		Triethyl aluminium	1,610	38.9
3	Polymerization of ethylene	Diethyl aluminium chloride	8,580	—
		Triethyl aluminium	No polymerization occurred	—
	Polymerization of propylene-(1)	Diethyl aluminium chloride	2,780	16.0
Triethyl aluminium		Polymerization scarcely occurred	—	
4	Polymerization of ethylene	Triethyl aluminium	280	—
	Polymerization of propylene-(1)	Triethyl aluminium	Polymerization scarcely occurred	—

Example 5.

To 10 g of the reaction solid prepared as described in Example 1, B were added 30 ml of hexane and 20 ml of ethyl aluminium dichloride, and the resultant mixture was allowed to react at 70°C for 2 hours. After the reaction mixture had been allowed to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 50 ml portions of hexane and dried to obtain a brown catalyst. Propylene was polymerized in the same manner as described in Example 1, E using the thus-obtained catalyst. Results obtained are shown in Table 3 below.

Example 6.

To 10 g of the reaction solid prepared as described in Example 1, B were added 25 ml of hexane and 10 ml of silicon tetrachloride, and the resultant mixture was reacted at 50°C for 2 hours. After allowing the reaction mix-

ture to stand to settle the precipitate, the supernatant was removed. The resultant precipitate was washed five times with 50 ml portions of hexane and dried to obtain a yellowish brown catalyst.

Polymerization of propylene was conducted in the same manner as described in Example 1, F using the thus-obtained catalyst. The results obtained are shown in Table 3 below.

Example 7.

To 5 g of the reaction solid prepared as described in Example 1, B were added 5 g of magnesium chloride, and the mixture was subjected to a ball mill treatment at room temperature for 5 hours to obtain a reddish brown catalyst.

Polymerization of propylene was conducted in the same manner as described in Example 1, F using the thus-obtained catalyst. The results obtained are shown in Table 3 below.

TABLE 3

Example	Polymerization method	Organoaluminium compound used in polymerization	Total amount of polymer produced per 1 g of catalyst	Total content of boiling heptane insoluble material
			(g)	(%)
5	Polymerization of propylene-(1)	Triethyl aluminium	1,970	62.4
6	Polymerization of propylene-(2)	Triethyl aluminium	490	78.3
7	Polymerization of propylene-(2)	Triethyl aluminium	296	72.2

WHAT WE CLAIM IS:—

1. A process for polymerizing an olefinically unsaturated hydrocarbon, which comprises polymerizing the olefinically unsaturated hydrocarbon in the joint presence of

(1) a catalyst obtained by reacting at a temperature of from -80 to 100°C, a transition metal compound represented by the formula



wherein Me represents a transition metal of Group IVb or Vb of the Periodic Table, X represents a halogen atom selected from fluorine, chlorine, bromine and iodine atoms, Y represents an oxygen atom or an organic radical selected from an alkyl group having 1 to 6 carbon atoms and alkoxy groups having 1 to 9 carbon atoms, n represents an integer

equivalent to or less than the maximum valence of said transition metal, and m represents a number having a positive value of from 0 to n (with the proviso that when Y is oxygen, then m is 1 and the number of said halogen atoms is $n-2$) with an organomagnesium compound, treating the resultant reaction solid with a Lewis acid and isolating the treated solid from the reaction mixture and (2) as an activator for the catalyst, an organo-aluminum compound represented by the formula



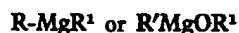
wherein Z represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, X represents a halogen atom as defined above, and n represents a number having a positive value of from 1.5 to 3.

2. A process as claimed in Claim 1, wherein said transition metal compound is selected from titanium tetrachloride, titanium tetrabromide, tetramethoxy titanium, tetraethoxy titanium, tetrapropoxy titanium, tetrabutoxy titanium, triethoxy titanium chloride, tripropoxy titanium chloride, tributoxy titanium chloride, diethoxy titanium dichloride, dipropoxy titanium dichloride, dibutoxy titanium dichloride, ethoxy titanium trichloride, propoxy titanium trichloride, butoxy titanium trichloride, dibutoxyethoxy titanium chloride, methyl titanium trichloride, vanadium tetrachloride, vanadium tetrabromide, vanadium oxychloride, vanadium oxybromide, zirconium chloride, zirconium bromide, niobium bromide, niobium chloride, tantalum chloride and tantalum bromide.

3. A process as claimed in Claim 1 or 2, wherein said organomagnesium compound is (1) a reaction product of magnesium in a metallic state and an organic compound represented by the general formula



wherein R represents a hydrocarbon radical selected from alkyl groups having from 1 to 18 carbon atoms and aryl groups having from 6 to 18 carbon atoms and X represents a fluorine, bromine, chlorine or iodine atom, reacted in the presence or absence of an inert diluent as a solvent, or (2) a compound represented by the formula



wherein R' and R¹ each represents a hydrocarbon radical selected from alkyl groups and aryl groups.

4. A process as claimed in any preceding Claim, wherein the reaction is conducted using from 0.5 to 3.0 moles of the organomagnesium compound per mole of the transition metal compound at a temperature of from -80 to 100°C.

5. A process as claimed in Claim 4, wherein the reaction used to prepare the catalyst was conducted using from 0.6 to 2.0 moles of the organomagnesium compound per mole of the transition metal compound at a temperature of from -30 to 80°C.

6. A process as claimed in any preceding

claim, wherein said Lewis acid is a halide or oxyhalide of a metal of one of Groups II to VIII of the Periodic Table, phosphorus or boron.

7. A process as claimed in Claim 6, wherein the Lewis acid is selected from ZnCl₂, CdCl₂, BF₃, BCl₃, BBr₃, AlCl₃, EtAlCl₂, Et₂AlCl, SiCl₄, SnCl₄, TiCl₄, TiBr₄, ZrCl₄, VCl₃, VCl₄, VOCl₃, WCl₆, MnCl₂, CoCl₂, NiCl₂, MgCl₂, PCl₃, POCl₃ and TeCl₄.

8. A process as claimed in any preceding claim, wherein the treatment with the Lewis acid was conducted by using from 0.1 to 10 moles of the Lewis acid per gram of the reaction solid.

9. A process as claimed in any preceding claim, wherein the treatment with the Lewis acid was conducted at a temperature of from -30 to 100°C for a period of more than 5 minutes.

10. A process as claimed in Claim 8 or 9, wherein the treatment was conducted at a temperature of from 0 to 80°C for a period of from 30 minutes to 5 hours.

11. A process as claimed in any preceding claim, wherein said organo-aluminium compound is diethyl aluminium chloride or triethyl aluminium.

12. A process as claimed in any preceding claim, wherein said catalyst is used in a proportion of from 0.001 to 100 moles per mole of said organoaluminium compound.

13. A process as claimed in any preceding claim, wherein said unsaturated hydrocarbon is a straight or branched chain hydrocarbon having from 2 to 15 carbon atoms.

14. A process for polymerizing olefinically unsaturated hydrocarbons, substantially as hereinbefore described with reference to any one of Examples 1 to 7.

15. A polymer when obtained by a process as claimed in any one of the preceding claims.

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